

## MERCURY CONTROL IN A WET SCRUBBER USING HYDROGEN SULFIDE

5 The subject matter of the present invention was developed under a research contract with the U.S. Department of Energy (DOE), Contract No. DE-FC22-94PC94251, and under a grant agreement with the Ohio Coal Development Office (OCDO), Grant Agreement No. CDO/D-922-13. The governments of the United States and Ohio have certain rights in the invention.

### *FIELD AND BACKGROUND OF THE INVENTION*

10 The present invention relates generally to the field of combustion and flue gas cleanup methods and apparatus and, in particular, to a new and useful method and apparatus for removing mercury from the flue gases generated during the combustion of fossil fuels such as coal, or solid wastes, through the use of hydrogen sulfide.

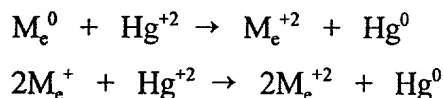
15 In recent years, the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency (EPA) have supported research to measure and control the emissions of Hazardous Air Pollutants (HAPs) from coal-fired utility boilers and waste to energy plants. The initial results of several research projects showed that the emissions of heavy metals and volatile organic carbons (VOCs) are very low, except for mercury (Hg). Unlike most of the other metals, most of the mercury remains in the vapor phase and does not condense onto fly ash particles at temperatures typically used in electrostatic precipitators and fabric filters. Therefore, it cannot be collected and disposed of along with fly ash like the other metals. To complicate matters, 20 mercury can exist in its oxidized ( $\text{Hg}^{+2}$ ) form, principally as mercuric chloride, ( $\text{HgCl}_2$ ), or in

its elemental ( $\text{Hg}^0$ ) form as vaporous metallic mercury. The relative amount of each species appears to depend on several factors such as fuel type, boiler combustion efficiency, the type of particulate collector installed, and various other factors.

The search for industrially acceptable methods for the capture of mercury from industrial flue gases has included a significant effort to determine how much mercury can be removed by existing, conventional air pollution control equipment. One device used in air pollution control is the wet scrubber, which is designed for the capture of sulfur oxides and other acid gases. Tests have been performed on several commercial scale and pilot scale wet scrubbers. These tests have produced some expected and some surprising results. It was generally expected that the oxidized mercury would be easily captured and the elemental mercury would be difficult to capture. These expectations were based on the high solubility of mercuric chloride in water and the very low solubility of elemental mercury in water. This expectation was generally fulfilled.

The surprising result concerned elemental mercury. Repeated tests during which the concentration of elemental mercury in the flue gas was measured revealed that more elemental mercury was leaving the wet scrubber than was entering.

One postulate proposed to explain the cause of the elemental mercury generation in the wet scrubber is described for example, by the following general reactions:



$\text{M}_e$  is any number of transition metals such as Fe, Mn, Co, Sn, . . .

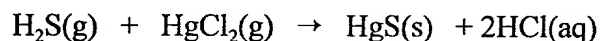
Transition metal ions are generally present in wet scrubber slurries as impurities in the industrial applications of concern. Thus, as the mercuric chloride is absorbed, a portion reacts with and becomes reduced by trace levels of transition metals and metal ions and because of its low solubility the elemental mercury is stripped from the liquid and returned to the flue gas.

Most of the recent efforts to capture and remove mercury from the flue gas produced by coal-fired units have concentrated on gas-phase reactions with introduced reagents such as activated carbon.

The subject of mercury emissions by the utility and waste to energy industries is a new area being investigated by both the DOE and EPA.

*SUMMARY OF THE INVENTION*

The present invention provides a means in the wet scrubber to rapidly precipitate the oxidized mercury at the gas/liquid interface in the wet scrubber before it can be reduced by the transition metals. One of the most insoluble forms of mercury is mercuric sulfide, which in mineral form is cinnabar. One means for supplying a source of sulfide for the oxidized mercury to react with is hydrogen sulfide. Thus, at the gas/liquid interface in the scrubber, the following reaction is proposed for the absorption and precipitation of ionized (oxidized) mercury:



HgS has a solubility product of  $3 \times 10^{-52}$  and therefore precipitates essentially completely. There is good reason to expect that the precipitation reaction proceeds faster than the reduction reactions. Specifically, in the case of the precipitation reaction, both reactants are well mixed in the gas phase. Thus, as they diffuse from the gas to the gas/liquid interface both reactants can react instantly at that interface. By contrast, the reduction reactions require that the reactants, i.e., the  $\text{Hg}^{+2}$  and the transition metal ion, diffuse in the liquid phase to a reaction plane in the liquid. Liquid phase diffusion is orders of magnitude slower than gas phase diffusion. Therefore, the oxidized mercury will rapidly precipitate as cinnabar in the scrubber and thereby prevent the reduction of that mercury back to vaporous elemental mercury. The precipitation of mercury as cinnabar has a distinct advantage over other mercury sequestering methods in that it converts mercury to a very insoluble form. In this way, the mercury should be inert and effectively removed from the food chain.

Accordingly, one aspect of the present invention is drawn to an improvement in a method using a wet scrubber for receiving and scrubbing an industrial gas containing mercury with a wet scrubber slurry, the improvement comprising: adding hydrogen sulfide to the industrial gas; and scrubbing the industrial gas in the wet scrubber. The method according to the present invention is particularly suited to the task of reducing mercury emissions in an industrial process which burns coal in a furnace to produce an exhaust flue gas, including conveying the exhaust flue gas through a dust collector and adding hydrogen sulfide to the flue gas before it enters the wet scrubber, or within the wet scrubber.

Another aspect of the present invention is drawn to an apparatus using a wet scrubber for receiving and scrubbing an industrial gas containing mercury with a wet scrubber slurry, and

particularly the improvement comprising: means for generating hydrogen sulfide; and means for supplying the hydrogen sulfide to the industrial gas upstream of the wet scrubber. The present invention is again particularly suited to utility installations which burn fossil fuels such as coal, or solid wastes, and which use, in addition to the wet scrubber, an electrostatic precipitator or a fabric filter and other conventional components for reducing emissions to the atmosphere.

Particularly, the present invention contemplates provision of a hydrogen sulfide generating system which produces the hydrogen sulfide from a reaction of adding an acid to a solution of aqueous sodium and/or potassium sulfide to generate the hydrogen sulfide. Advantageously, the hydrogen sulfide generating system may use equipment and methods wherein the acid is added to green liquor from the Kraft pulping process to generate the hydrogen sulfide.

The system has an inherent safety advantage in that no gas phase  $H_2S$  is accumulated or stored. All  $H_2S$  that is generated is immediately injected.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific benefits attained by its uses, reference is made to the accompanying drawings and descriptive matter in which a preferred embodiment of the invention is illustrated.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

In the drawings:

Fig. 1 is an illustration of the present invention as applied to a coal-fired utility boiler installation of the type used by utilities in the generation of electric power;

Fig. 2 is an illustration of a hydrogen sulfide  $H_2S$  generation system according to the present invention as particularly applied to a wet scrubber of Fig. 1;

Fig. 3 is an enlarged partial view of the circled area in Fig. 2, illustrating one embodiment of a system for injecting  $H_2S$  into flue gases for mercury control according to the present invention;

Fig. 4 is an enlarged partial view of the circled area in Fig. 2, illustrating another embodiment of a system for injecting  $H_2S$  into flue gases for mercury control according to the present invention;

Fig. 5 is a chart illustrating the results of tests comparing performance without  $H_2S$  injection to performance with  $H_2S$  injection; and

Fig. 6 is an illustration of the present invention as applied to a coal-fired utility boiler installation of the type used by utilities in the generation of electric power which employs a dry scrubber flue gas desulfurization system.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings generally, wherein like reference numerals designate the same or functionally similar elements throughout the several drawings, and to Fig. 1 in particular, Fig. 1 illustrates a coal-fired utility boiler installation of the type used by utilities in the generation of electric power, generally designated 10, and which represents one type of industrial process to which the present invention is applicable. In its broadest form, the present invention comprises a method for removing mercury from the flue gas generated during the combustion of fossil fuels or solid wastes through the use of trace amounts of hydrogen sulfide. Of course, while the aforementioned coal-fired utility boiler installations are but one example, and the method of the present invention will likely first find commercial application to the removal of mercury from the flue gases produced by such utility boiler installations which combust such fossil fuels, any industrial process using a wet scrubber type of absorber module to purify such flue gases may benefit. Such processes could include incineration plants, waste to energy plants, or other industrial processes which generate gaseous products containing mercury. Thus for the sake of convenience, the terms industrial gas, flue gas, or simply gas will be used in the following discussion to refer to any gas from an industrial process and from which an objectionable component, such as mercury, is to be removed.

As will be described *infra*, an alternate embodiment of the present invention involves methods and apparatus for the addition of trace amounts of hydrogen sulfide to industrial gases which are treated by dry scrubber flue gas desulfurization systems. Thus, while the majority of the following description is presented in the context of the present invention as being applied

to wet scrubber systems, it will be appreciated that the present invention is not limited thereto. Further, since both wet and dry scrubbers remove sulfur species from the flue gas by introduction of an alkali sorbent, some common terminology may be used as appropriate for the sake of convenience. In the case of wet scrubbers, the alkali sorbent can be provided as an aqueous alkali solution or slurry; in dry scrubbers, the alkali sorbent is usually provided as an aqueous alkali slurry. Thus, for the sake of convenience in the following description, the term aqueous alkali reagent will be used to encompass both aqueous alkali solutions and/or aqueous alkali slurries as appropriate to the type of scrubber means being used.

As illustrated in Fig. 1, and proceeding in the direction of flue gas flow generated during the combustion process, the boiler installation 10 includes a furnace 12 having a gas outlet 14 which conveys flue gases, generally designated 16, to an air heater 18 used to preheat incoming air 20 for combustion. Pulverizers 22 grind a fossil fuel 24 (e.g., coal) to a desired fineness and the pulverized coal 24 is conveyed via burners 25 into the furnace 12 where it is burned to release heat used to generate steam for use by a steam turbine-electric generator (not shown). Flue gas 16 produced by the combustion process are conveyed through the gas outlet 14 to the air heater 18 and thence to various types of downstream flue gas cleanup equipment. The flue gas cleanup equipment may comprise a fabric filter or, as shown, an electrostatic precipitator (ESP) 26 which removes particulates from the flue gas 16. A flue 28 downstream of the ESP 26 conveys the flue gas 16 to a wet scrubber absorber module 30 which is used to remove sulfur dioxide and other contaminants from the flue gas 16. Flue gas 16 exiting from the wet scrubber absorber module or, simply, the wet scrubber 30, is conveyed to a stack 32 and exhausted to atmosphere. Forced draft fans 34 and induced draft fans 36 are used to propel the air 20, fuel 24, and flue gases 16 through the installation 10. For further details of various aspects of such installations 10, the reader is referred to STEAM its generation and use, 40th Ed., Stultz and Kitto, Eds., Copyright © 1992 The Babcock & Wilcox Company, particularly to Chapter 35 - Sulfur Dioxide Control, the text of which is hereby incorporated by reference as though fully set forth herein. While the aforementioned STEAM reference contains a description of one form of wet scrubber 30 produced by The Babcock & Wilcox Company (B&W) and to which the present invention is applicable, the present invention is not limited to such B&W wet scrubber

designs. Persons skilled in the art will appreciate that the principles of the present invention apply equally well to other types of wet scrubber designs, available from other manufacturers.

The wet scrubber 30 contains, in a lower portion thereof, an inventory of wet scrubber slurry 38. During operation of the wet scrubber 30, recirculation pumps 40 pump and recirculate the wet scrubber slurry 38 up through pipes 42 and into absorber spray headers 44 located in an upper portion of the wet scrubber 30. The wet scrubber slurry 38 is sprayed counter currently into the flue gas 16 where it absorbs  $\text{SO}_2$ . The wet scrubber slurry 38 falls down through various devices and drains back into the lower portion of the wet scrubber 30. The scrubbed flue gas 16 then exits from a wet scrubber outlet 46 and is eventually conveyed to the stack 32.

Referring now to Fig. 2 in particular, there is shown an embodiment of a system for accomplishing the method of injecting small amounts of  $\text{H}_2\text{S}$  into flue gas for mercury removal according to the present invention. An  $\text{H}_2\text{S}$  generation system, generally referred to as 50, is provided and includes a well-stirred tank containing a liquid section 54 comprising sodium and/or potassium sulfide and a gas section 52 where air and  $\text{H}_2\text{S}$  are mixed and the mixture 74 of air and  $\text{H}_2\text{S}$  is transferred to an injection apparatus 76, described *infra*. The  $\text{H}_2\text{S}$  vapor pressure in the tank 51 is controlled by pH. The pH in the tank 51 liquid solution 54 is controlled by the addition of a strong mineral acid 56, such as hydrochloric or sulfuric acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ) from a tank or container 58, or by the addition of an alkali solution 57 such as sodium carbonate or sodium hydroxide ( $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$ ) from a tank or container 85. The acid is added to lower the pH and increase the  $\text{H}_2\text{S}$  vapor pressure in tank 51. The alkali is added to raise the pH and lower the  $\text{H}_2\text{S}$  vapor pressure in tank 51. The  $\text{H}_2\text{S}$  produced is immediately transported to the injection system 76. This is an inherent safety feature since no gaseous  $\text{H}_2\text{S}$  is allowed to accumulate. Stirring or mixing means, advantageously comprising a motor 64 and driven stirring shaft with two paddles 66, keep the tank sections 52 and 54 well stirred. As a result, the constituents in the liquid zone 54 are well mixed to yield the  $\text{H}_2\text{S}$  at the desired vapor pressure and the air 68 and generated  $\text{H}_2\text{S}$  are well mixed in the gas section 52. Pumping means 60 conveys the mineral acid 56 to the tank 51 via line 62; pumping means 61 conveys the alkali solution 57 to the tank 51 via line 63. Suitable control valves in lines 62 and 63 would be used as needed to control the flow of acid 56 and alkali 57.

Air 68 is provided by fan (blower or compressor) means 70 into the upper section 52 of tank 51 where it mixes with the H<sub>2</sub>S. Line 72 from the upper section of the tank 51 conveys the mixture 74 of air and H<sub>2</sub>S to an injection system 76 in flue 28 for injecting the H<sub>2</sub>S-air mixture 74 into the flue gas 16.

5 The rate of hydrogen sulfide generation is controlled by the rate of acid addition. The rate of air 68 provided into the tank 52 is controlled by the fan means 70 that supplies the air 68 in the quantity and at the pressure necessary for rapid mixing of the H<sub>2</sub>S-air mixture 74 with the flue gas 16 at an inlet 78 to the wet scrubber 30.

10 The H<sub>2</sub>S-air injection system 76 can comprise one or more pipes 78 arranged in a simple grid, each of the pipes 78 being provided with a plurality of apertures 80, the pipes 78 arranged across a width W and height H of flue 28, as shown in Fig. 3. Alternatively, the H<sub>2</sub>S-air injection system 76 could utilize a more sophisticated structure incorporating air foil mixing technology such as that illustrated in Fig. 4. In the system of Fig. 4, one or more air foils 82 would be provided, each having a plurality of slots or apertures 84 for introducing the H<sub>2</sub>S-air mixture 74 into the flue gas 16 as the flue gas 16 flows across the air foils 82. In either case, the flue gas 16 flowing past the pipes 78 or air foils 82 picks up the H<sub>2</sub>S-air mixture 74 and conveys it to the wet scrubber 30 to increase the H<sub>2</sub>S content in the flue gas 16 to a desired level, preferably between about 0.05 and 10 ppm, or more preferably 2 ppm or below.

15 Fig. 5 depicts test results obtained when a pilot scale wet scrubber was used to capture mercury. In Fig. 5, the legends "WS Inlet" and "WS Outlet" refer to conditions at the wet scrubber 30 inlet and outlet, respectively. The left two bars represent baseline conditions of the elemental mercury content of the flue gas 16 at the wet scrubber inlet and outlet, without H<sub>2</sub>S addition. The large increase in elemental mercury at the wet scrubber outlet is due to the chemical reduction of oxidized mercury within the wet scrubber 30 according to the reactions previously noted. The right two bars represent the improved performance achieved when H<sub>2</sub>S was injected at a concentration of about two parts per million (2 ppm). As shown, the chemical reduction of oxidized mercury to elemental mercury was completely prevented.

20 As described earlier and as illustrated in Fig. 6, the present invention is also applicable to combustion systems employing dry scrubbers for flue gas desulfurization. Again, like reference numerals designate the same or functionally similar parts. Flue gas 16 produced by



the combustion process are conveyed through the gas outlet 14 to the air heater 18 and thence to various types of downstream flue gas cleanup equipment. A flue 28 conveys the flue gas 16 to a dry scrubber absorber module 150 which is used to remove sulfur dioxide and other contaminants from the flue gas 16. Flue gas 16 exiting from the dry scrubber 150 is conveyed to a fabric filter or, as shown, an electrostatic precipitator (ESP) 26 which removes particulates from the flue gas 16 and then the flue gas 16 is conveyed to a stack 32 and exhausted to atmosphere. Forced draft fans 34 and induced draft fans 36 are used to propel the air 20, fuel 24, and flue gases 16 through the installation 10 as before.

Advantages of the present invention include the fact that the cost of control of mercury emissions according to the present invention is relatively insignificant compared to the costs for control of other hazardous air pollutants. Further, the amount of  $H_2S$  required should be below the threshold odor level. The cost and operating expenses of a system as depicted in Fig. 2 should be substantially less compared to any other system proposed to date. According to a preferred embodiment of the present invention, one source of the sodium sulfide used to generate the  $H_2S$  can comprise green liquor, an intermediate chemical used in the Kraft pulp and paper industry and which is readily available from pulp and paper companies. As is known to those skilled in the art, green liquor consists of an aqueous mixture of sodium sulfide and sodium carbonate. Green liquor is relatively easy and safe to handle and should be widely available.

According to the present invention, the mercury in the flue gas 16 ends up as mercuric sulfide (also known as cinnabar). This is the chemical form that mercury is most often found in nature and is probably the most desirable chemical form to sequester mercury. Much of the mercury in this form is present as a fine particulate in the scrubber slurry and for that reason, it is possible to separate much of the mercury from the gypsum crystals.

While a specific embodiment of the invention has been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles. By way of example and not limitation, while the principles of the present invention were described as being particularly applicable to fossil-fired boiler installations, it will be appreciated by those skilled in the art that the present invention can be used to remove mercury from industrial gases produced by refuse incinerators, refuse boilers, hazardous waste incinerators, or ore roasters.